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# Wide-band reflective films produced by side-chain cholesteric liquid-crystalline elastomers derived from a binaphthalene crosslinking agent

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#### ABSTRACT

A series of novel side-chain cholesteric liquid-crystalline elastomers based on polysiloxane and cholesterol derivate monomer were prepared by adopting a crosslinking agent containing binaphthalene group. The chemical structures and mesomorphic properties of the monomers and elastomers were confirmed by FT-IR, <sup>1</sup>H NMR, DSC and POM measurements. Worthily, the elastomers exhibited unusual temperature dependence of the helical twisting power (HTP) which is demonstrated resulting from coordination of the crosslinking agent and the mesogenic units. With increase in temperature, the HTP of elastomers containing small quantity of the crosslinking unit exhibited a turning point, while that of elastomers comprising much more crosslinking unit shifted straight. Furthermore, a single layer wide-band reflective film with non-uniform pitch distribution was prepared by utilizing the HTP variety of elastomers with change in temperature. From scanning electron microscopy (SEM) investigations, the mechanism of the broadband reflection was verified.

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# 1. Introduction

Liquid-crystalline elastomers (LCEs) have developed to be a new class of liquid crystal (LC) materials because of their special optical, mechanical and piezoelectric properties [1–3]. The polymer network structure of LCEs is usually produced by the introduction of crosslinking segment into LC polymer systems. And different crosslinkings can result in materials with distinct properties [4–6]. Recently, more and more researches have focused on cholesteric LCEs (ChLCEs) with helical structures [7–9], owing to their unusual piezoelectricity [10–16], tunable mirrorless lasing [17,18], and photonics [19,20]. Therefore ChLCEs exhibit potential applications in nonlinear optical materials, electro-optical materials and are considered as a candidate for the novel piezoelectric device.

In addition, since cholesteric liquid-crystalline polymers hold inherent characteristics of cholesteric LC (CLC), they have applications in wide-band reflective devices [21–29]. CLC possesses the unique properties of wavelength- and polarization- selective reflection when the molecules are macroscopically arranged in

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a periodic helicoidal structure [30,31]. The reflection wavelength,  $\lambda = nP$ , where  $n = (n_o + n_e)/2$  is the average of the ordinary  $(n_o)$  and extraordinary  $(n_e)$  refractive indices of the CLC, *P* is the cholesteric pitch corresponding to the length of a  $2\pi$  molecular rotation. For a wide-band reflective film, the reflection bandwidth  $\Delta\lambda = n_e P_{max} - n_o P_{min}$ , where  $P_{max}$  and  $P_{min}$  are the maximal and the minimal pitch length in the film, respectively. The pitch length is determined by the helical twisting power (HTP) of the CLC and given by  $P = [(HTP) \cdot Xc]^{-1}$ , here, Xc is the molar concentration of chiral component [32]. Consequently, information on the HTP of ChLCEs is the base for their application in wide-band reflective devices.

Binaphthol has been usually used as a chiral center for the synthesis of high HTP chiral dopant [33–35]. And studies on the synthesis of side-chain cholesteric liquid-crystalline polymers and networks derived from binaphthol are less reported. In this paper, a crosslinking agent containing binaphthalene group, a cholesteric monomer, and the corresponding side-chain ChLCEs were synthesized and characterized. The effect of the content of the crosslinking unit on the phase behavior and properties of the elastomers was discussed. Remarkably, the elastomers exhibited special and reversible HTP temperature dependence. And it is demonstrated that the ChLCE has great potential in making wide-band reflective films with non-uniform pitch distribution. Additionally, SEM was used to illustrate the mechanism of the broadband reflection.



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# 2. Experimental section

# 2.1. Materials

In this study, poly(methylhydrosiloxane) (PMHS, Mn = 390) was purchased from Sigma–Aldrich. 1,1'-binaphthyl-2,2'-diol, ethyl 4-

hydrozy benzoate, 3-bromoprop-1-ene, cholesterol and H<sub>2</sub>Pt<sub>6</sub>Cl were obtained from Sinopharm Chemical Reagent Co.Ltd. All solvents and reagents were purified by standard methods. Besides a nematic LC, SLC1717 ( $n_0 = 1.519$ ,  $n_e = 1.720$ , Slichem Liquid Crystal Material Co.Ltd.), a photo-polymerizable LC monomer, 1,4-di-[4-(6-acryloyloxy) hexyloxy benzoyloxy]-2-methyl benzene (C6M) and

# a Nematic LC: SLC1717

# Mixture of LCs with positive dielectric anisotropy

Photo-polymerizable LC monomer: C6M



Fig. 1. (a) Chemical structures of the materials used; (b) Synthetic routes of the mesogenic monomer and the crosslinking agent.

a photo-initiator, 2,2-dimethopxy-1,2-diphenyl-ethanone (IRG651, TCI Co.Ltd.) were used. C6M was synthesized according to the method suggested by Broer [36]. Fig. 1a shows the chemical structures of these materials.

#### 2.2. Synthesis of cholesteryl-4-allyloxybenzoate (M1)

M1 was synthesized according to the method reported in [37]. Yield: 78.5%. IR (KBr):  $v = 3080 \text{ cm}^{-1} (=C-H)$ , 2933, 2865 cm<sup>-1</sup> (-CH<sub>3</sub> and -CH<sub>2</sub>-), 1706 cm<sup>-1</sup> (C=O), 1645 cm<sup>-1</sup> (C=C), 1608, 1509, 1458 cm<sup>-1</sup> (Ar-), 1258 cm<sup>-1</sup> (C-O-Ar), 1173 cm<sup>-1</sup> (C-O-C). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 8.00-7.98$  (d, J = 8.4 Hz, 2H; Ar-H), 6.03–6.92 (d, J = 9.0 Hz, 2H; Ar-H), 6.06–6.03 (q, J = 6.6 Hz, 1H; CH<sub>2</sub> = CH-), 5.44 (d, J = 1.2 Hz, 1H; CH<sub>2</sub> = CH-), 5.41 (d, J = 1.2 Hz, 2H; = CH- in cholesteryl), 5.33–5.31 (q, J = 1.2 Hz, 1H; CH<sub>2</sub> = CH-), 4.84–4.82 (t, J = 4.8 Hz, 1H; -CH<sub>2</sub>-CHO-), 4.60–4.59 (d, J = 5.4 Hz, 2H; = CH-CH<sub>2</sub>O-), 0.93–2.46 (m, 43H; cholesteryl-H).

# 2.3. Synthesis of (S)-(-)-1, 1'-binaphthyl-2,2'-diyl bis(4-(allyloxy) benzoate (M2)

The synthetic route of crosslinking agent M2 is shown in Fig. 1b. 3-bromoprop-1-ene (220 mmol, 26.6 g) was added dropwise to a mixture of ethyl 4-hydroxybenzoate (200 mmol, 33.2 g), 200 ml of butanone, NaOH (220 mmol, 8.8 g) and KI (3 g) at room temperature and heated to 80 °C under magnetic stirred for 16 h. After filtration and removal of solvent, the residue was dissolved in 500 ml 10% NaOH and extracted twice by ether. After removal of ether, ethyl 4-(allyloxy)benzoate (1) was obtained. Then, a solution of 300 ml water and 20 g KOH were added to compound **1** at room temperature. The mixture was heated to 110 °C, refluxed for 10 h and acidified to PH 3.0 with hydrochloric acid. 32.4 g of white crystal 4-(allyloxy)benzoic acid (2) was obtained after several recrystallizations from ethanol. Yield: 91.0%. IR (KBr):  $v = 3025 \text{ cm}^{-1} (=C-H), 2965-2817 \text{ cm}^{-1} (-CH_2-, CH_2 = \text{and} = CH),$ 2678-2564 cm<sup>-1</sup> (-OH in -COOH), 1680 cm<sup>-1</sup> (C=O), 1605, 1510 cm<sup>-1</sup> (Ar-), 1252 cm<sup>-1</sup> (C-O-C). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 8.07 - 8.05$  (q, J = 1.8 Hz, 2H; Ar-H), 6.97-6.96 (q, *J* = 1.8 Hz, 2H; Ar-*H*), 6.09–6.03 (m, 1H; CH<sub>2</sub> = CH-), 5.46–5.42 (m, 1H;  $CH_2 = CH$ -), 5.34–5.32 (m, 1H;  $CH_2 = CH$ -), 4.63–4.61 (q, J = 3.0 Hz, 2H; = CH-CH<sub>2</sub>O-).

Compound 2 (31 mmol, 5.5 g), and thionyl chloride (65 mmol, 7.7 g) were added into a round flask equipped with an absorption instrument of hydrogen chloride. The mixture was heated to 90 °C and refluxed for 6 h. After removal of the solvent, 4-(allyloxy)benzoyl chloride(**3**) was obtained.(S)-(-)-1,1'-binaphthyl-2,2'-diol(15 mmol, 4.3 g) and pyridine (1.0 ml) were dissolved in 50 ml of dry THF to form a solution. The solution was added dropwise to compound **3**. heated to 90 °C and refluxed for 10 h. The mixture was cooled, filtered, poured in 200 ml of cold water and extracted twice by CH<sub>2</sub>Cl<sub>2</sub>. After removal of the solvent, the residue was purified by column chromatography (silica gel, ethyl acetate/petroleum ether = 1/1) to obtain 5.8 g of M2. Yield: 63.8%. IR (KBr):  $v = 3065 \text{ cm}^{-1}$  (=C–H), 2924, 2858 cm<sup>-1</sup>  $(-CH_2-, CH_2 = and = CH),1743, 1778 \text{ cm}^{-1} (C=O), 1645 \text{ cm}^{-1} (C=C),$ 1602, 1506 cm<sup>-1</sup> (Ar-), 1254 cm<sup>-1</sup> (C–O–Ar), 1158 cm<sup>-1</sup> (C–O–C). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS):  $\delta = 7.97 - 7.96$  (d, J = 9.0 Hz, 2H; Ar-H), 7.90–7.89 (d, J = 8.4 Hz, 2H; Ar-H), 7.80–7.79 (d, J = 9.0 Hz, 2H; Ar-H), 7.60–7.58 (d, J = 9.0 Hz, 2H; Ar-H), 7.56–7.55 (d, J = 9.0 Hz, 2H; Ar-H), 7.44 (s, 2H; Ar-H), 7.37 (s, 2H; Ar-H), 7.32 (s, 2H; Ar-H), 6.74-6.73 (d, J = 9.0 Hz, 4H; Ar-H), 6.00–5.99 (m, 2H; CH<sub>2</sub> = CH-), 5.39 (d, J = 1.8 Hz, 1H;  $CH_2 = CH_{-}$ ), 5.36 (d, J = 1.8 Hz, 1H;  $CH_2 = CH_{-}$ ), 5.29 (d, J = 1.2 Hz, 1H;  $CH_2 = CH_2$ , 5.28 (s, 1H;  $CH_2 = CH_2$ ), 4.51–4.50 (d, J = 4.8 Hz, 4H; = CH-CH<sub>2</sub>O-).



Fig. 2. Synthetic route and schematic representation of elastomers.

#### 2.4. Synthesis of the elastomers

For synthesis of elastomers E1-E4, the same method was adopted, and the synthetic route and schematic representation of elastomers are shown in Fig. 2. The content of crosslinking agent M2 increases gradually from E1 to E4. The polymerization experiments are summarized in Table 1. The synthesis of elastomer E2

Table 1				
Polymerization,	molecular weights	and polydisp	ersity indexes o	f elastomers.

Sample	Feed (mmol)		M2 <sup>a</sup> (mol%)	Yield (%)	Mn <sup>b</sup>	PDI <sup>b</sup>	
	PMHS	M1	M2				
E1	1.0	2.850	0.475	14.3	90	3744	1.44
E2	1.0	2.280	0.760	25.0	88	3356	1.43
E3	1.0	1.900	0.950	33.3	91	3171	1.40
E4	1.0	0.950	1.425	60.0	89	2975	1.38

<sup>a</sup> Molar fraction of M2 based on (M1 + M2).

<sup>b</sup> The apparent number-average molecular weight (*Mn*) and polydispersity index (PDI) were measured by GPC using PS standards.

was given as an example. LC monomer M1 (2.28 mmol, 1.24 g) was dissolved in 50 ml of dry, fresh distilled toluene. To the stirred solution, crosslinking agent M2 (0.76 mmol, 0.46 g), PMHS (1.0 mmol, 0.39 g) and 2 ml of H<sub>2</sub>PtCl<sub>6</sub>/THF (0.50 g of hexa-chloroplatinic acid hydrate dissolved in 100 ml of tetrahydrofuran) were added and heated under nitrogen and anhydrous conditions at 80.0 °C for 36 h. After removal of the solvent, the residue was dissolved in THF and precipitated in methanol, and dried under vacuum to obtain 2.1 g of elastomer E2. IR (KBr):  $v = 2949-2870 \text{ cm}^{-1}$  (–CH<sub>3</sub>, –CH<sub>2</sub>–), 1736, 1711 cm<sup>-1</sup> (C=O), 1604, 1510 cm<sup>-1</sup> (Ar-), 1077-1025 cm<sup>-1</sup> (Si–O–Si).

#### 2.5. Characterization and measurements

The synthesized compounds were characterized by FT-IR (Perkin Elmer Spectrum One) in solid state by the KBr method with wavenumber ranging from 400 to 4000 cm<sup>-1</sup> and <sup>1</sup>H NMR (Bruker DMX-600 spectrometer) with CDCl<sub>3</sub> as the solvent. The molecular weights of elastomers were estimated using gel permeation chromatography (GPC). The optical textures were observed by POM (Olympus BX51) with a hot stage calibrated to an accuracy of ±0.1 °C (Linkam THMS-600). The phase transition temperatures were investigated by DSC (Perkin Elmer Pyris 6) with a heating and a cooling rate of 10 °C min<sup>-1</sup> under a dry nitrogen purge. The morphology of the pitch distribution was observed by scanning electron microscopy (SEM, Zeiss EVO18).

### 2.6. Preparation of the mixtures and cells

The preparation of 1–7 mixtures is according to the way described bellow. The components of every mixture were dissolved in dichloromethane, and then sonicated for at least 2.0 h to ensure that an even mixture was obtained after removing the solvent. Mixtures 1–6 were prepared to characterize the HTP of monomers and elastomers. And mixture 7 was prepared to fabricate wideband reflective films.

To obtain homogeneous alignment of the mesogens, a 2.0 Wt% polyvinyl alcohol (PVA) aqueous solution was coated onto the inner surfaces of the substrates of the cells by spin casting (3000 rmin<sup>-1</sup> for 30s). The deposited film was dried at 80.0 °C for about 1 h, and subsequently rubbed with a textile cloth under a pressure of 2.0 g cm<sup>-2</sup> along one direction to make the polymer oriented. As the liquid crystal mesogens are club-shaped, they can be



Fig. 3. FT-IR spectra of monomers and elastomers.

induced to arrange as the direction of the oriented polymeric film [38,39]. 40- $\mu$ m-thick PET (polyethylene terephthalate) films were used as spacer of the cells. The monomers and elastomers were filled into the cells by capillary action at their mesophase temperature ranges.

The wide-band reflective films were prepared by carrying out the following procedure. The cell containing mixture 7 was irradiated with UV light (5 mW cm<sup>-2</sup>, 365 nm) for 30 min at 100 °C, during which polymer network was formed from the photopolymerization of C6M. Then it was cooled slowly to 70 °C and quenched below the melting temperature of mixture 7. Finally properties of the cell were tested at room temperature.



**Fig. 4.** <sup>1</sup>H NMR spectra of elastomers E1–E4.

Table 2		
Thermal pro	perties of monomers and elastomers	•

Compound	Tm₁ (°C)	Tm <sub>2</sub> (°C)	Ti (°C)	$\Delta T^{a}$
M1	115.2	-	235.1	119.9
M2	7.0 <sup>b</sup>	54.3	_	_
E1	51.1	-	145.0	93.9
E2	45.8	-	138.0	92.2
E3	42.7	135.0	_	_
E4	43.0	130.0	_	_

<sup>a</sup> Mesophase temperature ranges.

<sup>b</sup> Glass transition temperature of M2.

# 3. Results and discussion

3.1. <sup>1</sup>H NMR and FT-IR characterization of monomers and elastomers

As shown in Fig. 1b, mesogenic monomer M1 and crosslinking agent M2 were synthesized in four steps. The structures of monomers were confirmed by FT-IR and <sup>1</sup>H NMR spectra. The FT-IR spectra of M1 and M2 showed characteristic olefinic C=C at  $1645 \text{ cm}^{-1}$ , ester C=0 band at 1706 cm<sup>-1</sup> for M1, 1743 and  $1778 \text{ cm}^{-1}$  for M2 as can be seen from Fig. 3. Yields, detailed polymerization and molecular characteristics of elastomers are summarized in Table 1. The apparent number-average molecular weight (Mn) of elastomers decreases gradually with the increase of the concentration of the crosslinking unit. Elastomers E1-E4 were synthesized by a one-step hydrosilylation reaction between the Si-H bond of PMHS and the olefinic C=C bond of monomers to form Si–C–C bond. After the reaction finishing, the olefinic C=C bond is consumed and its stretching band should disappear in the FT-IR spectra of elastomers. The FT-IR spectra of E1-E4 are shown in Fig. 3. They showed the complete disappearance of Si-H stretching at 2160 cm<sup>-1</sup> and olefinic C=C stretching band at about 1645 cm<sup>-1</sup>. Characteristic Si-O-Si stretching bands appeared at 1200-1000 cm<sup>-1</sup>. In addition, the absorption bands of ester C=O

(1706–1738 cm<sup>-1</sup>) and aromatic (1608-1506 cm<sup>-1</sup>) still existed. These characteristics suggested the successful incorporation of monomers onto the polysiloxane chains for all the elastomers. <sup>1</sup>H NMR can provide an effective method for verification in the synthesis of LCEs [40]. As can be seen in Fig. 4, the augment of the peak area during 6.0–8.5 ppm corresponding to aromatic C–H proton and the abatement of the peak area corresponding to methyl, methylene proton in 0.0–3.0 ppm well reflected the changes with increasing the concentration of crosslinking agent M2 from E1-E4.

# 3.2. Thermal and texture analysis

The thermal properties of the monomers and elastomers listed in Table 2 were determined by DSC and POM measurements. From DSC results, a melting transition and a cholesteric-isotropic phase transition for M1 appeared at 115.2 and 235.1 °C; a glass transition and a melting transition for M2 occurred at 7.0 and 54.3 °C, respectively. POM results showed that M1 exhibited enantiotropic cholesteric phase, while M2 revealed no texture and birefringence on heating and cooling cycles. As M1 was filled into a homogeneous treated cell, it presented planar texture of cholesteric phase when heated upon 115.2 °C, and focal-conic texture of cholesteric phase when cooled from its isotropic state as shown in Fig. 5a and b.

Fig. 6 shows the DSC thermograms of elastomers E1-E4. In the DSC curves, a melting temperature (Tm) can be detected. The value of Tm decreases with increasing crosslinking content from E1 to E4. From POM measurements, a melting temperature (Tm) and a clearing temperature (Ti) were observed for E1 and E2. During the temperature range between Tm and Ti, they exhibited cholesteric phase textures as shown in Fig. 5c and d. Two kinds of melting temperatures were seen by POM observations for E3 and E4. The first melting temperature (Tm<sub>1</sub>) is consistent with the melting temperature detected on the DSC curves. Both E3 and E4 changed to be isotropic state when heated to the second melting temperature (Tm<sub>2</sub>). All the thermal information for the elastomers obtained



Fig. 5. Optical textures of monomers and elastomers: (a) oily streak texture of M1 on heating to 130.3 °C; (b) focal-conic texture of M1 on cooling to 224.9 °C from its isotropic state; (c) planar texture of E1 at 117.0 °C; (d) planar texture of E2 at 127.0 °C.

from DSC and POM measurements are summarized in Table 2. As seen from the data in Table 2, adopting small quantity of crosslinking units in the elastomers did not markedly affect their mesomorphic behaviors [41], and reversible LC phase transitions can be observed as a result of enough molecular motion. For example, both E1 and E2 exhibited wide mesophase temperature ranges. However, when the content of the crosslinking agent is up to about 30.0 mol%, such as for E3 and E4, LC phase disappears owing to the depression of LC orientational order.

# 3.3. HTP analysis of monomers

It is well known that a CLC can also be formed by doping a chiral dopant into a nematic LC. As mentioned before, the pitch length of CLC,  $P = [(HTP) \cdot Xc]^{-1}$ , where HTP and Xc are the helical twisting power and molar concentration of the chiral dopant, respectively. Therefore, HTP of monomers and elastomers could be characterized by measuring the pitch lengths of CLCs induced by them, when the Xc is unchangeable. The pitch lengths were measured by the Cano wedge technique [42]. In this measurement, a wedge-shaped cell (KCRK-07, Japan) with a wedge angle,  $\theta$  (0.01937 rad), was used and the inner surfaces of its two glass substrates were treated to provide a homogeneous orientation of the LC molecules. After the mixture was filled into the cell, a Grandjean-Cano texture formed with disclination lines separated by a distance L. The pitch length P is determined from  $P = 2Ltan\theta \approx 2L\theta$ . When Xc is small, the pitch length is long and easily measured as the disclination lines are clear and regular. So the smaller weight ratio of the chiral dopant is helpful for the pitch length measurement. Here, we prepare mixtures 1-6 by doping about 2 Wt% monomer or elastomer into the nematic LC SLC1717. The compositions, weight ratios, phase transition temperatures and corresponding enthalpy changes of the mixtures are listed in Table 3.

Fig. 7a shows the temperature dependence of the pitch length of mixture 1. It can be found that the pitch length decreases from 12.24 to 9.07  $\mu$ m with increasing temperature from 20 to 93 °C, which also can be seen from the corresponding POM micrographs of mixture 1 in the cell inside Fig. 7a. Then from mixture 1 and combining the formula  $P = [(HTP) \cdot Xc]^{-1}$ , it can be concluded that the HTP of monomer M1 increases greatly with increasing temperature.

The temperature dependence of the pitch length of mixture 2, a CLC induced by crosslinking agent M2, is shown in Fig. 7b. The pitch length increases from 1.84 to 3.02  $\mu$ m when heating from 20 to 80 °C. The results indicated that the HTP of M2 decreases with



Fig. 6. DSC thermograms of elastomers on the first heating at 10 °C min<sup>-1</sup>.

#### Table 3

The compositions, weight ratios, phase transition temperatures and corresponding enthalpy changes of mixtures 1–7.

Mixture (type)	Weight ratio	$T_{\text{Ch-I}} (^{\circ}\text{C})^{c}$	$\Delta H (J g^{-1})^d$
1	2.0/-/-/-/98.0 <sup>a</sup>	94.6	0.71
2	-/2.0/-/-/-/98.0 <sup>a</sup>	84.0	0.68
3	-/-/2.0/-/-/98.0 <sup>a</sup>	91.1	0.86
4	-/-/-/2.0/-/-/98.0 <sup>a</sup>	93.0	0.67
5	-/-/-/2.0/-/98.0 <sup>a</sup>	89.8	0.93
6	-/-/-/2.0/98.0 <sup>a</sup>	88.0	0.50
7	95.99/4.0/0.01 <sup>b</sup>	116.5	3.63

<sup>a</sup> Weight ratio: M1/M2/E1/E2/E3/E4/SLC1717.

<sup>b</sup> Weight ratio: E1/C6M/IRG651.

<sup>c</sup>  $T_{Ch-I}$ : Clearing temperature from cholesteric to isotropic phase.

<sup>d</sup>  $\Delta$ H: Delta H from cholesteric to isotropic phase.

the increase of temperature. From above discussion, it is clear that with increase in temperature the HTP of M1 increases, while that of M2 decreases; and the HTP of M2 is greatly larger than that of M1. In other words, monomer M1 and crosslinking agent M2 have opposite temperature dependence of HTP. Hence the HTP of elastomers grafting both M1 and M2 is possible to exhibit distinct phenomenon.

# 3.4. HTP analysis of elastomers

Fig. 8 shows the temperature dependence of the pitch lengths of mixtures 3–6. When heating the pitch lengths of mixtures 3 and 4 increase firstly and then decrease; while those of mixtures 5 and 6



**Fig. 7.** Temperature dependence of the pitch length of mixture 1 (a) And mixture 2 (b); the insets are the corresponding POM micrographs taken in the Cano wedges at 20 and 93 °C for mixture 1, 20 and 80 °C for mixture 2, respectively.



Fig. 8. Temperature dependence of the pitch lengths of mixtures 3-6.

increase all through the temperature range. This illustrates that with increase in temperature the HTP of E1 or E2 decreases firstly and then increases; while that of E3 or E4 exhibits a straight increase. It is noticeable that the pitch length increases more smoothly and the temperature for it decreasing enhances in sequence from mixture 3 to mixture 4.

A possible explanation for above phenomena is given considering both contributions of M1 and M2 segments on the HTP temperature dependence of elastomers. On one hand, as the HTP of M2 is larger than that of M1, the HTP of elastomers increases with increasing the content of M2 from E1 to E4. Correspondingly, the pitch length of mixtures decreases from mixture 3 to mixture 6 as shown in Fig. 8a. On the other hand, owing to the opposite temperature dependence of HTP for M1 and M2, the HTP of E1 or E2 exhibits a turning point from decreasing like that of M2 to increasing because of the function of M1 with increasing temperature. So the pitch length of mixture 3 or mixture 4 increases firstly and then decreases with increasing temperature, as shown in Fig. 8 (b) and (c). For example, the pitch length of mixture 3 increased from P<sub>1</sub> (18.5  $\mu$ m) to P<sub>2</sub> (20.6  $\mu$ m) from 20 to 70 °C, while decreased to P<sub>3</sub> (19.9  $\mu$ m) when heated to 90 °C as shown in Fig. 9.

Accordingly, the HTP of E1 increases with increasing temperature up to 70 °C. As the M2 fraction increases, the HTP of elastomers decreases at high temperature. And when it is up to about 30.0 mol %, the turning point disappears. In other words, the HTP of E3 or E4 decreases straight and the pitch length of mixture 5 or mixture 6 increases all along with increase in temperature as seen from Fig. 8 (d) and (e). So the pitch length of mixture 6 increased from P<sub>4</sub> (3.9  $\mu$ m) to P<sub>6</sub> (6.3  $\mu$ m) when heated from 20 to 85 °C, as shown in Fig. 10. From above discussion, it can be concluded that owing to coordination of M1 and M2 segments, the HTP of elastomers exhibits special thermally sensitive properties, which is important for their application in display areas.

#### 3.5. Application of elastomers in wide-band reflective films

As the HTP of the synthesized ChLCEs is temperature dependent discussed above, their pitch lengths exhibit temperature dependence correspondingly. So their selective reflection wavelengths can shift with changing temperature. Fig. 11 shows that the transmittance spectrum of E1 shifts to shorter wavelength with the increase of temperature. And the reflection wavelengths are located



Fig. 9. Schematic representation and POM photographs of mixture 3 in the wedge-shaped cell with increasing temperature.



Fig. 10. Schematic representation and POM photographs of mixture 6 in the wedge-shaped cell with increasing temperature.

in 704, 580, 480 and 424 nm at 70, 90, 110, and 130 °C, respectively. Then broadband reflective films may be obtained by using the property of the synthesized elastomers.

Mixture 7 was prepared to fabricate wide-band reflective films. Fig. 12 shows that the reflection wavelength of mixture 7 exhibits an obvious blue shift with increasing temperature from 70 to 100 °C. The reflection band broadened to about 251 nm from 430 to 681 nm after UV-curing at 100 °C. A possible explanation to this phenomenon is given considering the HTP variety of the ChLCE at different temperatures and the anchoring effect of the polymer network. Fig. 13 shows the schematic representation of the rearrangement of the ChLCE molecules in mixture 7 when temperature changes. At high temperature, the mixture was filled into a homogeneously treated cell and exhibited uniform short pitch as shown in Fig. 13a. Then ChLCEs in some local regions were fixed in this short pitch by polymer networks formed from the photopolymerization of C6M after UV-curing. When cooling, as the HTP of E1 decreases with decreasing temperature up to 70 °C as mentioned before and the anchoring effect of the polymer network was not strong enough, the pitch length of ChLCEs in the regions far away from the polymer network becomes long. And benefiting from the polymer property hold by the ChLCEs, this long pitch was frozen after quenching the cell below its melting temperature (33 °C). As a result, a non-uniform pitch distribution was formed in the film as shown in Fig. 13b. Also, as the UV light irradiates the whole cell, non-uniform pitch distribution presents in the whole film.

It has been reported that SEM can be used to detect the pitch of CLCs [30,43]. Due to the anchoring effect of the polymer network, it can template the cholesteric order and pitch distribution of



Fig. 11. The transmission spectrum of E1 shifts to shorter wavelength as temperature increases.



Fig. 12. The transmission spectra of mixture 7 before and after UV-curing.



**Fig. 13.** Schematic representation of the rearrangement of ChLCE molecules in the cell containing mixture 7 when temperature changes. (a) Before UV-curing at high temperature; (b) After UV-curing at high temperature and cooled to low temperature under the melting temperature of mixture 7.

liquid crystals. The micro-structure of the helical polymer network in a wide-band reflective film has been reported widely [44,45]. So the non-uniform pitch distribution of mixture 7 was observed with SEM to demonstrate the mechanism described above. Fig. 14 shows the micro-structure of the fractured surface of the irradiated cell containing mixture 7. The dimension of the three bands in the fine structure on the fractured plane is P, corresponding to a  $2\pi$  cholesteric molecular rotation. It can be seen that different pitch lengths, changing gradually from about 0.24  $\mu$ m ( $P_1$ ) to about 0.38  $\mu$ m ( $P_5$ ), distributed randomly in the fractured plane and  $P_1 < P_2 < P_3 < P_4 < P_5$ . According to the equation,  $\lambda = nP$ ,  $\lambda_1$  should be 430 nm while  $\lambda_5$  should be 681 nm in theory. This demonstrates that the HTP variety of the synthesized ChLCEs with the change of temperature and polymer networks formed at high temperature can induce a non-uniform pitch distribution and confirms above explanation of the mechanism.



**Fig. 14.** SEM image of the fractured surface of cross-linked mixture 7. The dimension of the three bands in the fine structure on the fractured plane corresponds to a  $2\pi$  molecular rotation, that is, *P*. Different regions exhibited diverse pitch lengths, and  $P_1 < P_2 < P_3 < P_4 < P_5$ .

#### 4. Conclusion

In this paper, we described the synthesis and characterization of series of side-chain ChLCEs containing cholesteryl-4а allyloxybenzoate as mesogenic unit and (S)-(-)-1, 1'-binaphthyl-2,2'-diyl bis(4-(allyloxy)benzoate as chiral crosslinking unit. The elastomers containing less than 25.0 mol % of crosslinking units showed reversible cholesteric phase and wide mesophase temperature ranges. Furthermore, HTP temperature dependences were studied. With increase in temperature, the HTP of M1 increased and that of M2 decreased, which induced that the HTP of elastomers containing less than 25.0 mol% of the crosslinking unit exhibited a turning point (from decreasing to increasing), while that of elastomers comprising much more crosslinking unit increased all along when heating. In addition, wide-band reflective films were prepared by utilizing the HTP variety of the synthesized ChLCEs with the change of temperature. And the SEM studies suggested that a non-uniform pitch distribution has formed in the film. In view of practical applications, these robust broadband reflective films may be attractive for reflective LC displays, brightness enhancement films and smart switchable reflective windows.

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# References

- [1] Kishi R, Sisido M, Tazuke S. Macromolecules 1990;23:3779-84.
- [2] Zentel R. Angew Chem Adv Mater 1989;101(10):1437–45.
- [3] Loffler R, Finkelmann H. Macromol Chem Rapid Commum 1990;11:321-8.
- [4] Meng FB, Zhang BY, Liu LM, Zhang BL. Polymer 2003;44:3935–43.
- [5] Hu JS, Zhang BY, Zhou AJ, Yang LQ, Wang B. Eur Polym J 2006;42:2849-58.
- [6] Hu JS, Zhang BY, Zheng YY, Li QY. React Funct Polym 2005;64:1-11.
- [7] Sawa Y, Ye F, Urayama K, Takigawa T, Gimenez-Pinto V, Selinger RLB, et al. PANS 2011;108:6364–8.

- [8] Serra F, Matranga MA, Ji Y, Terentjev EM. Opt Express 2010;18:575-81.
- [9] Hirota H, Ji Y, Serra F, Tajbakhsh AR, Terentjev EM. Opt Express 2008;16:5320-31. [10] Hirschmann H, Meier W, Finkelmann H. Makromol Chem Rapid Commun 1992;13:385-94.
- [11] Pleiner H, Brand HR. | Phys II 1993;3:1397–409.
- [12] Terentjev EM. Euro Phys Lett 1993;23:27–32.
- [13] Pelcovits RA, Meyer RB. De Physique II 1995;5:877-82.
- [14] Brehmer M, Zentel R. Mol Cryst Liq Cryst 1994;243:353–76.
- [15] Kelly SM. J Mater Chem 1995:5:2047-73.
- [16] Terentjev EM, Warner M. Eur Phys | B 1999;8:595-601.
- [17] Finkelmann H. Adv Mater 2001:13:1069–72.
- [18] Schmidtke J, Stile W, Finkelmann H. Phys Rev Lett 2003;90:083902.
- [19] Cicuta P, Tajbakhsh AR, Terentjev EM. Phys Rev E 2002;65:051704.
- [20] Bermel PA, Warner M. Phys Rev E 2002;65:056614.
- Mitov M, Boudet A, Sopena P. Eur Phys J B 1999;8:327-30. [21]
- [22] Xiao JM, Zhao DY, Cao H, Yang H. Liq Cryst 2007;34(4):473-7.
- [22] Mitov M, Binet C, Boudet A. Mol Cryst Liq Cryst 2001;358:209–23.
  [24] Zografopoulos DC, Kriezis EE, Mitov M, Binet C, Phys Rev E 2006;73:061701.
- [25] Xiao JM, Cao H, He WL, Ma Z, Geng J, Wang LP, et al. J Appl Polym Sci 2007;  $105 \cdot 2973 - 7$
- [26] Fan B, Vartak S, Eakin JN, Faris SM. Appl Phys Lett 2008;92:061101.
- [27] Fan B, Vartak S, Eakin JN, Faris SM. J Appl Phys 2008;104:023108.
- [28] Li L, Faris SM. Proceeding of the SPIE 1996;2873:202–5.
- [29] Witte PVD, Brehmer M, Lub J. J Mater Chem 1999;9:2087-94.

[30] de Gennes PG, Prost J. The physics of liquid crystals. New York: Oxford University; 1993.

5845

- [31] Lam L. In: Kitzerow H, Bahr C, editors. Chirality in liquid crystals. New York: Springer; 2001. p. 159.
- Kumar G, Neckers D. Chem Rev 1989;89:1915-37. [32]
- [33] Akagi K. Chem Rev 2009;109:5354-401.
- [34] Guo RW, Li KX, Cao H, Wu XJ, Wang GJ, Cheng ZH, et al. Polymer 2010;51: 5990-6.
- [35] Guo RW, Cao H, Liu HJ, Li KX, Huang W, Xiao JM, et al. Liq Cryst 2009;36(9): 939-46.
- [36] Broer DJ, Boven J, Mol GN, Makromol Chem 1989:190:2255-68.
- Ì37Ì Adams NW, Bradshaw JS, Bayona JM, Markides KE, Lee ML. Mol Cryst Liq Cryst 1987:147:43-60.
- [38] Geary JM, Goodby JW, Kmetz AR, Patel JS. J Appl Phys 1987;62(10):4100-8.
- [39] Sato Y, Sato K, Uchida T. Jap J Appl Phys 1992;31:L579-81.
- [40] Ambrogi V, Giamberini M, Cerruti P, Pucci P, Menna N, Mascolo R, et al. Polymer 2005:46:2105–21.
- [41] Noel C, Shibaev VP, Baron M, Hess M, Jenkins AD, Jin J, et al. Pure Appl Chem 2001:73(5):845-95.
- Cano R, Soc B, Mineral F. Crystallogr 1968;91:20-7. [42]
- [43] Hu W, Zhao HY, Song L, Yang Z, Cao H, Cheng ZH, et al. Adv Mater 2010;22: 468-72
- [44] Broer DJ, Lub J, Mol GN. Nature 1995;378:467-9.
- [45] Bian ZY, Li KX, Huang W, Cao H, Yang H. Appl Phys Lett 2007;91:201908.